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Sustainability and biophysics basis of technical and economic processes: A survey of the reconciliation by thermodynamics

Moisés Teles dos Santos *, Song Won Park

Department of Chemical Engineering, Polytéchnic School, Universidade of São Paulo, Av. Prof. Luciano Gualberto, n. 380, trav. 3, CEP 05508-900, São Paulo-SP, Brazil

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A B S T R A C T

In spite of the existence of a generalized debate about sustainable development, the natural constraints imposed by the irreversibility nature of technical and economic transformations are normally less discussed. The Second Law of thermodynamics (Entropy Law) reveals the unidirectional and irreversible aspect of such transformations, and it can be used as an auxiliary tool to deal with sustainability assessment. The exergy, a concept derived from entropy, can offer qualitative measurements of resources depletion and environmental impact not covered by mass or energy. This opens opportunities to enrich the sustainability discussion. The multiple interactions among the ecosystem, the economic environment and the technical level are highlighted, along with discussions about how the entropy concept has improved the description of the three levels. The aim of this paper is to review the environmental sustainability concept from the perspective of entropy law, offering a survey of relevant applications of exergy available in literature.

Contents

* Corresponding author. Tel.: +55 11 3091 2237, 55 11 3091 2246; fax: +55 11 3813 2380.
E-mail addresses: teles.msantos@gmail.com, moises.telesdossantos@ensiacet.fr (M. Teles dos Santos).

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1. Introduction

The population growth, the increasing standards in the consumption of modern societies, their impact on the ecosystems and the limited resources on earth are major drivers for more sustainable process and products. Process Systems Engineering has experience and tools to cope with both (process and products), but the boundaries must be broader beyond process and product level to correctly deal with sustainability challenges.

Fundamental questions normally underestimated are: given the current level of economic activity and consumption standards (on which relies the whole industrial sector), are they sustainable? How to effectively measure the degree of sustainability of a process or product? The aim of this article is offer an up-to-date survey of relevant studies in addressing these questions, emphasizing what we call "the metabolic dimension" of sustainability and how thermodynamics is useful to access this dimension.

The consensual definition of sustainable development is that of the Brundtland Report produced by the World Commission on Environment and Development [1]: that providing human needs without compromising the ability of future generations to meet their own needs. It is also well-established that sustainability has three pillars: economic viability, social concerns and ecological issues (the "triple botttom line"). To anticipate the conclusion of this article, we point out that these "three pillars" are not pillars at all in the sense that they do not have the same importance in supporting sustainability, but there is rather a hierarchical relation between them, caused by the biophysical nature of economic activities.

Sustainability is a multidisciplinary concept that must involve engineering, biology, economics, ethics and social sciences. Considering the multiple interactions among these areas, sustainability assessment must take into account the entire system, rather than focus its analysis and conclusions in individual subsystems. As highlighted by Bakshi and Fiksel [2], the boundaries of "the process" must be expanded, beyond the industrial and the corporation level. This approach aims to capture the true resources consumption and waste generation as a whole, improving the evaluation of how sustainable the human activities are.

The sustainability assessment has claimed for the development of criteria and indicators definitions that can be used for measurement, evaluation and comparison of industrial activities impacts on the environment [3,4]. The ultimate objective of sustainability assessment is, according to Ness et al. [4], to provide decision-makers with an evaluation of global to local integrated nature–society systems in short and long term perspectives. Once a coherent evaluation is offered, the choice of the actions to be made to move towards more sustainable process can be more rational.

In previous works, we discussed how exergy-based tools match some of the 12 principles of "Green Engineering" [5,6]. In the following sections, the discussions about the usefulness of thermodynamic-based tools (entropy and exergy) and the role of the Second Law of Thermodynamics on sustainability assessment are expanded.

2. Multilevel approach for sustainability assessment

Earth is a large-scale complex system composed of a number of subsystems interacting and functioning together, exchanging mass and energy flows. If the goal is to reduce emissions, decrease waste and resource consumption, we must broaden the control volume of the system under study. If each domain is designed independently to match a set of local sustainability standards, it may be possible that sustainability requirements in one domain conflict with another and that the overall system is less sustainable than it could be [7]. A simple illustrative example is the boy that cleans his bedroom throwing the trash into his sister's bedroom. If the control volume is the boy's bedroom, it became cleaner; however, the girl's bedroom became dirtier. Considering the house as a whole, nothing has changed or it can even be worse.

Fig. 1 shows the different systems interacting with each other in the planet. It must be highlighted that Fig. 1 shows subsystems embedded in another system; they are not considered as separated "dimensions" of sustainability, which is commonly the case.

Material and energetic fluxes from ecosystems feed the economic environment (process A–B). This economic environment is composed mainly of public and private companies, which are influenced by political issues (not covered in Fig. 1). The economic environment distributes raw-materials (resources) for a large variety of economic agents, including industries (process B–C). Inside the companies, the raw-materials are used on technical transformations (process C–D), where technology and internal accumulated knowledge convert them into products (process D-E). These products have an economic value in the company's level (F) and go through the economic environment (process F–G).

Recovery, recycling and reuse allow using these outputs as inputs for the same or another process. However, the production and consumption of these products and services generate wastes and emissions that cannot be reused and are sent back to the ecosystem (process G–H). Can the flux G–H be null? This question

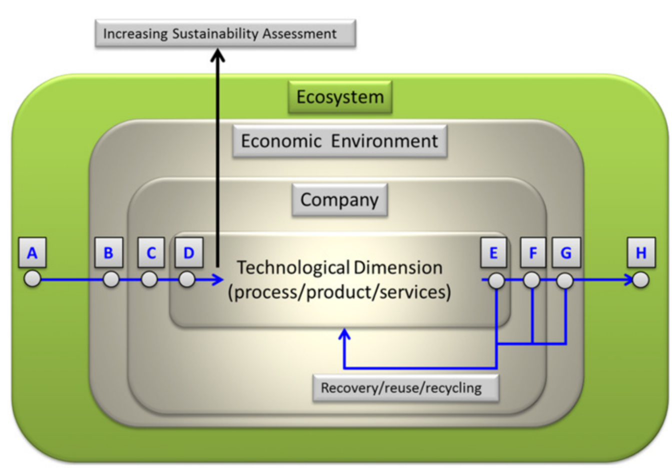

Fig. 1. Multilevel system comprising human activities in modern societies. The social level is represented by its economical component.

is further discussed in Section 6, but we anticipate that the Second Law of Thermodynamics imposes irreversibilities that cannot be overcome without an environmental effect.

The discussions about sustainability must move towards the higher levels in Fig. 1. Indeed, Process System Engineering has already made progress in shifting towards upper levels, moving from the traditional focus on the industrial process to a broader focus on the chemical supply chain, including safety, environmental factors and economics [2]. However, expanding these spatial boundaries implies a higher degree of complexity and uncertainty associated with the available data.

A theory of sustainable systems must deal with large non-linear dynamic and complex systems. According to Ottino [8], a complex system is a system with a large number of agents capable of exchanging stimuli with one another and with their environment. The common characteristic of all complex systems is that they display organization without external organizing principle being applied. In the most elaborate examples, the agents can learn from past history and modify their states. Also, the knowledge of the elementary building blocks does not mean knowledge of the behavior of the global system. Alterations can occur on part of the system, but the system may still function [8]. We can observe these characteristic thorough different levels in Fig. 1.

We believe that facing the challenges that emerge from the modeling of complex systems can better address the sustainability agenda than efforts to address very localized solutions for specific problems. Even if we consider only the technological level, improvements in one system do not necessarily lead to overall improvements. For example, in energy conversion systems, the so-called “Coefficient of Structural Bonds” [9] show that improvements in the performance of one equipment can be counterbalanced by an equal or greater reduction in performance of other elements, in such a way, that the overall plant efficiency can remain unchanged or worse.

On the ecosystem level, much progress has been made to develop models to assist environmental management and describe the biosphere dynamics due to anthropogenic impact: stochastic models, structurally dynamic models, statistical models, fuzzy models, based on catastrophe theory, population dynamic models, bio-geo-chemical models, spatial distribution models, individual-based models, artificial neural network models, artificial intelligence, chaos theory and static models [10,11]. Also, a variety of ecological indicators was developed, aiming to assess the condition of the environment or to monitor trends over time [12]. These authors highlight the importance of accurately defining ecological indicators that are economically viable and non-conflicting.

Ten years ago, it was stated that exergy analysis and ecological economics can be useful in including the ecosystem level [2]. We extend this discussion in the next sections and we make an overview of the advances in this area.

3. Entropy and sustainability assessment: a natural relationship

3.1. Exergy as a measure of departure from environment

Even nowadays, many people seem to believe that the input necessary to drive process is energy. If it was the case, we could reuse waste as input for the same process, as the energy is always a conserved quantity. The energy is only converted from one form to another, but it cannot be created or destroyed (First Law of Thermodynamics). This is a quantitative principle, where no concerns about the directions or feasibility of such conversions are made.

Some simple examples:

- A piece of ice in a hot sunny day losing heat to the environment and spontaneously keeping itself cold does not violate the First Law, if the amount of energy lost by the ice is equal to the amount of energy delivered to the surroundings. However, the real world shows that natural transformations have a spontaneous direction and the inverse direction cannot be performed unless an external source of energy is supplied to the system. In this example, the spontaneous process is that energy from environment heats the ice, until a thermal equilibrium is reached. The inverse process (cooling ice) is possible only if an external flow of energy is used (as in refrigeration processes). The sense of “direction” of transformations spontaneously occurring in nature is revealed by entropy and the Second Law of Thermodynamics. Entropy is a property of the system that always increases in a real and spontaneous process.
- A glass is being broken. There is no mass or energy changes in the glass. However, it is evident that a broken glass has a lower economic value.
- Diamond and graphite. These materials are made by the same chemical element, carbon. However, the crystalline state of diamond has lower entropy (higher ordered state) and its economic value is much greater than that of graphite.

In the previous examples, it is impossible to regenerate the lower entropy state (initial state) without using external resources from the surroundings. They are irreversible processes. One can observe that an entire glass can be regenerated from a broken one (apparently a reversible process). However, it is impossible to do that without consumption of energy from the surroundings (to melt the glass and regenerate the original form). Thus, from the thermodynamic point of view, recycled materials in irreversible processes always leave a “trace” on the environment.

Even if an external source of low entropy energy is carried into the system and the entropy of this system decreases, this is followed by an external increase of entropy of surroundings, in such a quantity that the positive variation on entropy of the surroundings is greater than the negative variation of the system entropy (in absolute values), and the total entropy variation remains positive. Irreversible processes always have a cost.

Natural (biological, ecosystems, and societies) and artificial systems (equipments, industries) are open systems supported by low-entropy flows. Within those systems, irreversible transformations take place, leading to entropy generation. As only a part of the input flows are converted into useful flows, wastes with higher entropy are always sent back to the environment. The fact that only a part of these feeding flows can be used is imposed by the Second Law of Thermodynamics.

Exergy (an entropy-based concept) provides a measure of usefulness or quality of material and energy fluxes to run processes and the exergy balance can identify process irreversibilities, which can be used as a thermodynamic parameter of sustainability assessment [13,14].

Exergy is based on simultaneous energy and entropy balances and can be defined as the maximum amount of work when a system is brought to thermodynamic equilibrium with the environment, in terms of temperature, pressure and composition, through reversible processes [15]. Exergy quantifies the departure of the characteristics of a system in relation to its environment (Fig. 2).

In Fig. 2, the “potential” accumulated in system A (exergy of system A) represents the maximum work obtainable by taking system A through reversible processes to the equilibrium with the environment. After reaching equilibrium with its environment in terms of temperature and pressure ($T_A = T_0$, $P_A = P_0$), system

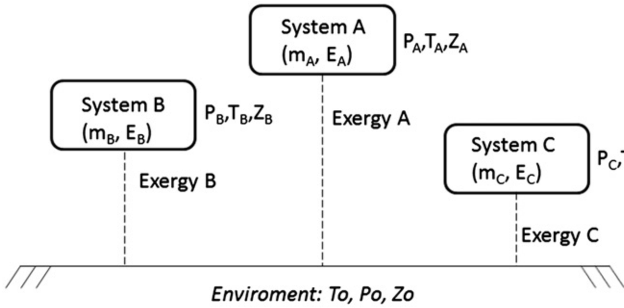

Fig. 2. Schematic view of exergy as a measure of departure from the environment in terms of temperature, pressure and chemical composition. *m*: mass; *E*: energy; *P*: pressure, *T*: temperature; *Z*: chemical composition.

A still has a "potential" to perform work (chemical exergy), if the chemical composition of system A is different from that of the environment ($Z_A \neq Z_0$).

Chemical exergy is then the work that can be obtained by taking a system which has the parameters T_0 and P_0 to the chemical equilibrium with the commonly appearing components of the surrounding nature [16].

The more the temperature and pressure of a system differ from the temperature and pressure of the environment (T_0, P_0), the higher is its physical exergy.

Notice that systems A, B and C can have the same mass ($m_A = m_B = m_C$) and the same energy content ($E_A = E_B = E_C$); what indicates how far they are from environment conditions is the exergy, which is related to the "quality" of this energy content. In this sense, E_A has a larger "quality" or economic value than E_B, which in turn has a larger "quality" than E_C.

When the physical and chemical equilibrium with the environment (dead state) is achieved, systems (A, B or C) do not have any more driving forces to conduct processes.

Therefore, exergy analysis requires the definition of a reference state. A characteristic of the natural systems is that the reference state is difficult to define and does not comply with the theoretical requirements of a reference state: it is not in equilibrium and has local and time gradients. For a further discussion about the reference state definition, we recommend the paper of Rosen and Dincer [17]. Despite the difficulties in establishing a reference state that comply with the theoretical issues, Szargut et al. [15] established a standard composition normally adopted in exergy analysis. This was further revised and updated for some metals [18].

3.2. Exergy balance

Although energy cannot be created or destroyed, it can be degraded in quality, reaching a state in equilibrium with its surroundings and hence of no further use for performing tasks. The Second Law of Thermodynamics (entropy balances) contributes with significant information, identifying, locating and quantifying irreversibility through the entropy generated. The Second Law of Thermodynamics shows that part of the energy (in a process stream or natural resource) is not available for use due to the entropy generation that always occurs in the conversion processes.

Actually, the maximum potential to cause change (exergy) illustrated in Fig. 2 is measured by evaluating how the enthalpy and entropy of the system differ from the corresponding values for the same system if it was in the conditions of the environment.

A linear combination between the First and Second Laws of Thermodynamics (energy and entropy balances) for an open system, with m material streams entering, n material streams leaving the system and p heat transfers, with no significant changes in kinetic and potential energy leads, in steady state, to

$$\sum_{i=1}^{m}[\dot{m}_{in}(\overline{h}_{in}-T_0\overline{s}_{in})]_i-\sum_{i=1}^{n}[\dot{m}_{out}(\overline{h}_{out}-T_0\overline{s}_{out})]_i = \dot{W}+T_0\dot{S}_g+\sum_{i=1}^{p}\dot{Q}_i\left(1-\frac{T_0}{T_i}\right) \quad (1)$$

where $\dot{m}$ is the mass flow (kg/s), $\overline{h}$ is the specific enthalpy (kJ/kg) and $\overline{s}$ is the specific entropy (kJ/kg K).

The second term of this equation is the maximum amount of available work due to the change from the initial (in) to the final conditions (out) of temperature and pressure. In this term, the quantity $T_0\dot{S}_g$ is the lost work (Gouy-Stodola Theorem). This loss is due to entropy generation ($\dot{S}_g$), caused by process irreversibilities. In the particular case where a stream achieves physical equilibrium with environment (T_0, P_0) through reversible processes ($\dot{S}_g=0$), the work obtained is the maximum possible and represents the total physical exergy of the stream. Thus, the physical exergy ($\overline{b}_{ph}$) for a stream is given by

$$\overline{b}_{ph}=\overline{h}(P,T)-\overline{h}(P_0,T_0)-T_0[\overline{s}(P,T)-\overline{s}(P_0,T_0)] \quad [\text{kJ/kg}] \quad (2)$$

The general exergy balance can be written as

$$\sum_{i=1}^{m}\dot{B}_e=\sum_{i=1}^{n}\dot{B}_s+\dot{I} \quad [\text{MW}] \quad (3)$$

where $\dot{B}_e$ represents the exergy flows entering the system, $\dot{B}_s$ the exergy flows that are leaving the system and $\dot{I}$, the exergy destruction rate. These flows can be material or associated to heat transfer, once heat transfers contribute to entropy variation. For systems in physical equilibrium with the environment (temperature and pressure) but with different compositions, there is a remaining potential, which can be used to cause changes. The chemical exergy ($\overline{b}_{ch}$) is defined as

$$\overline{b}_{ch}=\sum_{i=1}^{q}x_i(\mu_{0i}-\mu_{0i}^{*}) \quad [\text{kJ/kg}] \quad (4)$$

where x_i is the mole fraction of the component i in the system, μ_{0i} is the chemical potential of each component and μ_{0i}^{*} the chemical potential of the substance (or reference substances) on defined environmental conditions. For solid and liquid organic systems the chemical exergy can be correlated with the elementary composition (atomic ratio of chemical elements), the moisture content and the lower heating value. This is the case of biomass used in the example shown in Appendix A.

The main characteristic of Eq. (3) is its non-conservative nature. In other words, in a real process, although mass and energy are conserved, their usefulness (exergy) is destroyed due to the entropy generation (irreversibility) in this process. Appendix A illustrates the use of Eqs. (1)–(3).

4. Applications

4.1. Depletion of natural resources evaluation

Resources are materials in non-equilibrium with the environment (exergy content). The exergy of a natural resource can be interpreted as a measure of its "usefulness". This is the useful value of resources, not fully described by energy or mass. The resource consumption can be even defined as exergy removal from the environment [19,20,21].

The degradation of natural resources is a form of environmental damage. Minimizing the depletion of these natural resources is one of the principles of sustainable engineering [22]. Thus, exergy can be used as an auxiliary tool for sustainability indication of renewable resources, as highlighted by Omer [23]. An interesting concept that arises from this discussion is the "thermo-ecological

cost", defined as the cumulative consumption of non-renewable exergy due to the production of a particular product, including the consumption due to the necessity of compensation of environmental losses caused by rejection of harmful substances to the environment [24,25]. This indicator will be further discussed in Section 7.2.

Wall and Gong [26] pointed out that environmental pollution is an inevitable consequence of the use of deposit resources and the depletion of these resources may not be the most serious problem, but rather the emission of toxic substances that end up in the environment. Exergy is a common measurement of both processes A–D and E–H in Fig. 1, and thus offers additional information about the level of natural resources consumption.

4.2. Evaluation of impacts on ecosystems

Being a measurement of the departure of the state of a system from that of the environment, exergy can be used as an indicator of impact. As commented by Kotas [9], in a general way, the larger the exergy of a pollutant, the larger the disturbance caused on environmental equilibrium. The exergy content of an emission represents the maximum potential to cause changes in the environment until the emission (matter or energy) reaches total equilibrium with this environment.

By definition, material and energy flows possess exergy only when in disequilibrium with a reference environment and the exergy content of waste emissions is more meaningful than the corresponding energy content as a measure of potential impact [27].

Ecosystems are composed of abiotic factors (soil, light, water and air) in a high level of organization, equilibrium and interaction with biotic factors (plants, animals and microorganisms). Environmental pollution can be interpreted as any interference in the ecosystem equilibrium through material or energy streams. Such streams cause large unbalances due to differences concerning the environmental parameters (temperature, pressure and composition). Exergy, better than energy, reflects these differences between waste and the environment where it is discharged. Further discussions about ecosystem evaluation by exergy can be found in the book of Dincer and Rosen [28].

Seager and Theis [29] exemplify different forms of exergy embodied in a material stream: the concentration gradient between concentrated pollutants and a dilute reference environment, thermal, physical, radioactive (including light) and vibrational (such as noise). Therefore, different forms of exergy may be dissipated in the environment and it may be postulated that there are quantitative relationships between different forms of waste exergy and environmental impact [29]. Although the relationships between exergy and toxicity are not well established, exergy is a more realistic indicator than either mass or waste heat, which is the only information obtained by conventional analysis [30].

4.3. Industrial use

Increasing efficiency of industrial processes is an important way to reduce costs, resources usage and environmental emissions. The exergy analysis can reveal the margin available to design more efficient energy conversion systems. Although the maximum efficiency in energy conversion systems corresponds to an ideal process (no entropy generation, reversibility) and all real processes are, in some extension, entropy generators, an exergy analysis can point out how far from ideality a process is, and thus, indicate the potential for improvements.

For energy conversion systems, many studies using exergy analysis have been done for evaluation and optimization [31,32] and evaluation of environmental impacts [33]. Many cases in different types of industries can be found in the literature: sugarcane and ethanol industry [34–37], petrochemicals [38–43], hydrogen [44] and biofuel production [45,46], pulp and paper mills [47–49], vegetable oils plants [50,51] and ammonia synthesis [52]. There are also works aiming to include exergy analysis in process simulators to optimize processes taking into account exergy losses [40,53,54].

We have also performed an exergy analysis of 2 different cogeneration systems in a pulp and paper mill. In this work, the overall efficiency in energetic (quantitative) basis is 81.55%; if a qualitative basis is used (exergy content of resources and products), the overall efficiency is 24.89%. The main sources of irreversibility (entropy generation) were localized and quantified: 73.85% of exergy of fuels is destroyed in boilers, due to the combustion and heat exchange processes, which are highly irreversible [55].

This list is not exhaustive in any sense and the literature on industrial uses of exergy increases continually.

Improvements in process efficiencies can lead to the same level of production and services with less consumption and depletion of natural resources. Therefore, exergy, as an auxiliary tool for industrial optimization, also represents a potential tool to achieve more sustainable systems. For energy systems, exergy can be noted as an auxiliary tool for process integration aiming to maximize the use of available energy streams in the process. Some cases in this area can be found in the works of Serra et al. [35] and in a methanol plant [56]. As stated by Rivero [40], it is necessary to go beyond the classical quantitative methods to calculate the efficiency of the process and identify where and how energy is degraded in its quality on industrial systems.

Exergy can be therefore related to sustainable development through efficiency improvements and environmental impacts reduction in the industrial level.

4.4. Exergetic life cycle assessment

The efforts to expand the boundaries beyond process level on Fig. 1 led to the development of the Life Cycle Analysis (LCA), a holistic approach to cope with environmental performance of a product, based on its entire life cycle, including raw material acquisition, production process, use and disposal. LCA is useful to identify material and energetic flows consumed and produced during the entire life-time of a product. However, one of the limitations of this method is that it cannot evaluate different emissions in regard to environmental effects on the same basis [57].

According to Ayres et al. [30], there are three major advantages of using exergy in LCA: (1) It provides a common measure of inputs and outputs and allows the estimation of exergetic efficiency, which is an indication of potential improvements. (2) It facilitates the comparison between different materials in relation to environmental impacts. (3) It facilitates reporting and monitoring environmental indicators of companies and countries over time.

Exergy can help to quantify resources depletion, waste emissions and process losses. Following this idea, there is an increasing number of works dealing with the so-called Exergetic Life Cycle Analysis (ELCA). Some examples can be found in power generation [58], hydrogen production [59], coal gasification and aluminium production [60]. More recently, Portha et al. [43] showed the usefulness of exergy concept coupled with LCA to evaluate the environmental impacts in catalytic reforming process of petrochemical industry. Cornelissen and Hirs [61] made a comparative study between information supplied by LCA and by ELCA, showing the importance of exergy for determining consumption and depletion of natural resources.

4.5. Countries and economic sectors

Some works cope with the use of exergy for evaluating fluxes on an entire country's economy. Some examples are analysis of industrial sector of China [62] and Norway [63], residential and

commercial sector of Japan [64], Greek transport sector [65], United States [66] and United Kingdom [67], to cite a few and more recent examples. Also, countrywide economy evaluation on an integrated approach can be found [68–70].

One important concept that arises from this area of study is the emergy, proposed by Odum [71]. According to this theory, different forms of energy (materials, human labor and economic services) can be evaluated on the common basis of biosphere by converting them into equivalents of only one form of energy, the solar kind, expressed as solar equivalent Joule (seJ).

4.6. Biological systems

Entropy can be used as a measure of disorder of a system (the Boltzmann approach). In this sense, all things in the universe obey the Second Law of Thermodynamic, tending to a state with higher disorder (increased entropy). Live systems, however, are a "contradiction" to this universal tendency. They show a high level of organization, order and complexity, maintaining their departure from the environment conditions. However, there are constant gradients (temperature, pressure and chemical composition) between the living system and its environment. The spontaneous process would be, therefore, the reduction of these gradients: the live system in equilibrium with the environment. So, how can living systems maintain their differences from the environment, "violating" the entropy law? The answer is that living systems use external sources as low-entropy inputs and discharge high-entropy outputs into the environment. For further reading on thermodynamic principles of living and non-equilibrium systems, the fundamentals works of Schrodinger [72] and Prigogine [73] (both Nobel Prizes) and more recently, Schneider and Kay [74] are recommended.

The analogy between biological systems and the economic system, keeping their organization by low entropy fluxes, developed by Georgescu-Roegen [75] is revisited and well discussed by Cechin [76].

The exergy analysis of a biochemical process is, in principle, not different from that of a technological process. However, as demonstrated by the work of Lems [77], one important difference is that determining the exergy of biochemical compounds in living cells implies accounting for the effects of complex intracellular environments in which thousands of compounds interact with each other. The complexity increases, but the principles are the same. Exergy analysis for live systems modeling can be found recently for photosynthesis [78] and for human body metabolism [79]. We can observe that the entropy concept and the Second Law of Thermodynamics offer a versatile tool in evaluating energy conversion systems, where the useful part (exergy) drives process, whether it is a technical system (e.g. a turbine of Appendix A) or a biological one.

Actually, all systems in Fig. 2 have the spontaneous tendency to go to an equilibrium state with the environment (increase entropy principle). Maintaining a local violation of the increase entropy principle is possible only due to the consumption of low entropy resources from the environment and generating wastes with higher entropy back to the environment.

5. Second law and economic implications for sustainability assessment

5.1. Economic environment vs. ecosystem

The relationships between the economic environment and the ecosystem (Fig. 1) have been a source of paradigm changes in economic sciences [76].

In the conventional description of the economic process, there is no integration in terms of inputs and outputs between the economic environment and the ecosystem of Fig. 1. The economy is viewed as a circular flow of goods and services, self-sufficient, similar to the perpetual motion machine, which is not feasible according to physical laws.

Georgescu-Roegen, in his work "The Entropy Law and the Economic Process" [75], highlighted that the economic process is not the circular closed system as described in the neoclassical approach, but rather an open process integrated into nature, consuming resources of low entropy and generating wastes of high entropy. In this point of view, the economic process is rather a unidirectional process in non-equilibrium, a dynamic system directly integrated into nature. Once the ecosystem is integrated into the description of the economic environment, the sustainability discussion can be better addressed and the need for a multilevel approach of Fig. 1 is highlighted.

Recognizing that the economic process has a "metabolic" dimension that obeys natural laws, Georgescu's ideas (based on entropy) offer a more realistic description of how economic activities interact with the environment. The biophysical basis of economy, illustrated in Fig. 1, is therefore, integrated into the economic theory,

On an industrial level, the entropy has also economic implications. Many researchers have recommended that costs are better distributed among outputs based on exergy. The so-called thermoeconomics, second-law costing and exergoeconomics methods have performed economic analyses based on exergy [80–83]. The main reason to distribute costs among outputs using exergy is that exergy is a consistent measure of economic value.

5.2. Economic environment vs. technological dimension

It is clear from Fig. 1 that the technological dimension is completely embedded in the economic dimension. The economic system comprises the economic parameters such as prices, market prospects and cost of resources. According to these parameters, the economic merit of a new technology can be estimated, given a set of demand conditions for the product and the supply of production factors. The technological system is related to technical aspects of process and products, such as the chemical composition and the process to be used to manufacture goods. The search procedure described by Evolutionary Theory in the economic area highlights the stochastic relationships and the uncertainties associated of the two dimensions: the economic attributes cannot be perfectly predicted from technological ones [84]. Also, unless we talk about pure science, all innovations occurring on the technical level in Fig. 1 must match the economic environment goals (higher level). As discussed by Dosi [85], the technological trajectories occur inside economic trade-offs.

The ultimate consequence of such considerations is that no improvements on the technological system are feasible if they are not economically feasible. Improvements on products and process made in the technological system aiming to achieve "sustainability" are subordinated to economic constraints.

6. Recycling

According to Principle 6 of the so-called "The Twelve Principles of Green Engineering", a measure is required that is able to account for the quality losses during recycling [86]. These quality losses cannot be measured by mass balances, as the quality degradation cannot be translated by mass measures alone [87]. Exergy is then proposed as a measure of the efficiency of recycling process.

Castro et al. [88] showed a practical case of recovery/recycling of metals where exergy revealed losses not identified using mass or energy. They showed that the entropy of the alloys increased

because contaminations were introduced during recycling. These contaminations interfere in the material's structure and can also react with the other compounds, originating a 'less ordered' structure (quality loss). To dilute this contamination and bring the material back to the original quality, high purity resources are needed. Clearly in this example, the specific exergy content of the alloys decreased during the recycling steps and the recovery of the original state of the metal is possible only using external exergy sources (environment cost).

But, a question arises: to what extent can the rejects be recycled? Or in a similar way, can the flux G–H in Fig. 1 be null? There are two schools of thought addressing this question.

Georgescu-Roegen [75] stated that perfect recycling is impossible, whence matter becomes dissipated and loses its quality, in the same way that occurs for energy (second law).

There is no controversy that an external source of exergy is necessary for recycling matter. The controversy is about if the external source of exergy of Earth (the sun) is sufficient to allow perfect and perpetual recycling of wastes.

For Georgescu-Roegen, the answer is no: perpetual recycling would be impossible, even if unlimited high-quality energy (exergy) was available, because of entropic dissipation. This is not yet a scientific consensus. The critics to this proposition argue that the earth is not a thermodynamically closed system and the continuing flux of exergy from the sun suffices to permit materials recycling forever.

Ayres [89] critiques the Georgescu's approach using the idea of a "wastebasket": although the recovery processes are admitted to be never with 100% of efficiency, the author argues that the waste from the recovery process simply goes back to the "wastebasket". If this "waste pile" is big enough, it is possible to compensate for the losses. This author states that the total recycling of materials is perfectly consistent with the second law of thermodynamics, if an external source of exergy is provided (e.g. the sun), and the correct interpretation of limits to recycle is that not all of the materials in the earth can be in 'active service' at the same time (the recovery process itself will generate wastes).

This discussion about limits to recovering materials goes far beyond the technological dimension and has fundamental implications in the economic paradigm of growth and development.

Indeed, these two schools of thought represent two current approaches that must be studied to properly address the sustainability problem in the upper levels of Fig. 1:

- School (1) represented by the initial ideas of Frederick Soddy (Nobel prize), followed by Georgescu's work and their followers (Herman Daly, John Gowdy and Charles Perrings);
- School (2) represented by the energetic school of Howard Odum, Frederick Cottrell, Malcolm Slesser and Robert Costanza. The ideas of Robert Solow and Joseph Stiglitz (Nobel prizes) concerning the role of natural resources in economic activity are also in opposition to Georgescu's approach.

Thus, the answer for the previous question is open. Taking into account this conflict of ideas seems fundamental to better address the issues of sustainability. The Process System Engineering (PSE) community must be aware of this debate. If economics has incorporated thermodynamic insights, the PSE community must go through upper levels of Fig. 1, using its knowledge on modeling of large and complex systems.

We believe that discussions about the possibility of perpetual recycle of materials must take into account a better knowledge of the phenomenon of hysteresis, present in materials as polymers, metals and lipids. Hysteresis is the dependence of a system not only on its current state but also on its past state. It is a kind of "memory" showed by some materials and it is often associated with irreversible changes. "Memory", path dependency and irreversibility are, indeed, related to the unidirectional aspect of natural transformations that obey the entropy law.

7. Metrics for sustainability assessment

7.1. General classification

Ness et al. [4] made a large inventory of sustainability assessment tools and they classified them based on the spatial focus, temporal characteristics and nature–society integration. Three main categories could be identified: (1) indicators/indices (quantitative data that represent economic, social and/or environmental variables in a defined region); (2) product-related assessment (focus on different flows in relation to a specific product or service, rather than a region, e.g. LCA and exergy analysis) and (3) integrated assessment (tools used to improve the basis for policy-making and project approval).

On a macroscale level (countries/regions), indicators and indices are often used tools. They include a large set of socio-economic and environmental variables such as forest damage, fishing pressure, tourism intensity, waste landfilled, water quality, education levels and population growth rates [4]. Among them, there are indices that attempt to develop alternatives to the national accounting (Gross Domestic Product—GDP and Net National Product—NNP). These last ones, although with their widely adopted use as a measure of economic growth of countries (an in this sense, a major criteria in comparing countries and guiding public policy), show a lack of considerations about environmental issues or quality life. Some examples of indices that try to cover environmental factors are the Sustainable National Income—SNI, The Index of Sustainable Economic Welfare—ISEW, the General Progress Indicator—GPI, the Adjusted Net Savings (world bank) and The Ecological Footprint [4].

7.2. Thermo-ecological cost

Szargut and co-authors [24,25,90,91] proposed the use of the "thermo-ecological cost". This cost is based on the cumulative consumption of non-renewable exergy in the fabrication of a particular product. Given its amplitude, we describe it further.

Eq. (5) shows a general expression to account for the Thermo-ecological cost of a product A [24]:

$$\rho_A = \tau_n\left(\sum_j \dot{G}_j\rho_j + \sum_k \dot{P}_k\zeta_k - \sum_u \dot{G}_u\rho_i s_{iu}\right) + \frac{1}{\tau}\left[\sum_m G_m\rho_m(1-u_m) + \sum_r G_r\rho_r\right] \tag{5}$$

This equation takes into account 3 fundamental aspects when accessing sustainability: construction, operation and decommissioning of the process necessary to produce A. Table 1 summarizes each term in Eq. (5).

7.2.1. Operational thermo-ecological cost

The first term accounts for the flux associated to the raw materials, semi-finished products or energy carriers supplied to the process. The second term accounts for the exergy consumption of non-renewable resources for compensation of the results of the emission of the *k*th waste product. The third term accounts for replacement of current products by means of by-products generated. Therefore, the operational thermo-ecological cost contains all the non-renewable exergy that feeds the process plus the exergy needed for mitigation of wastes discharged on environment minus the positive effect of by-products production.

Table 1
Parameters used for thermo-ecological cost calculation.

Operational thermo-ecological cost	Construction and decommissioning thermo-ecological cost
$\dot{G}_j$,ρ_j [kg/s],[J/kg]: nominal flow rate and specific thermo-ecological cost of jth raw-material, semi-finished product and energy feeding the process	G_m,ρ_m [kg],[J/kg]: amount and specific thermo-ecological cost of mth material/energy carrier used for the construction of installation
$\dot{P}_k$,ζ_k [kg/s],[J/kg]: nominal flow rate and specific thermo-ecological cost of kth waste discharged on environment	$(1-u_m)$: portion of material m used for construction not reusable
$\dot{G}_u$,ρ_i,s_{iu}[kg/s],[J/kg]: nominal production rate of uth by-product, specific thermo-ecological cost of ith product replaced and replacement ratio	$G_r\rho_r$[kg][J/kg]: expected consumption and specific thermo-ecological cost of rth material/energy carrier used in repairs.
τ_n[s/year]: annual operation time of the installation	τ[year]: nominal life time of the installation

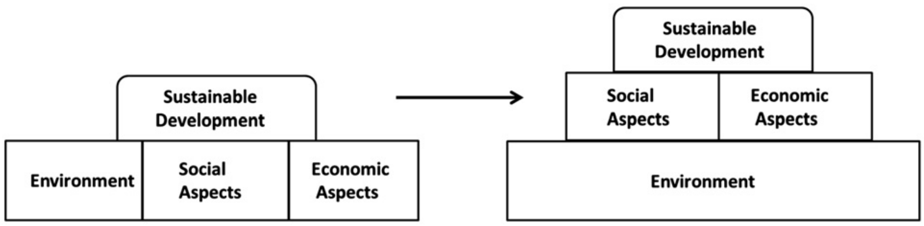

Fig. 3. Transition from the "triple bottom line" point of view to the hierarchical relation between the three main determinants of sustainable development.

7.2.2. Construction and decommissioning thermo-ecological cost

There are 2 terms: the first one is the thermo-ecological cost of materials and energy carriers used for the construction of the installation (G_m, ρ_m) and the second one is related to thermo-ecological cost of materials and energy used in repairs (G_r, ρ_r). However, the utilization of materials remaining after the wear and dismantling of the installation can reduce the depletion of non-renewable resources used on installation. This is accounted by the recovery factor um.

7.2.3. Sustainability index

The thermo-ecological cost (ρ) can be evaluated in comparison to the exergy content in the final product (b) (Eq. (6)). This ratio is called sustainable index and its value depends on how much renewable exergy is used. When there is a large use of renewable resources (low thermo-ecological cost), the value can be smaller than 1. Values greater than 1 indicate that more non-renewable exergy was used than the exergy content of final product, indicating a non-favorable scenario.

$$r = \frac{\rho}{b} \tag{6}$$

A very simple example is given in Appendix B. For further details, the reader must consult the works of Szargut and co-workers [24,25,90,91].

The main advantages of the use of the thermo-ecological cost are: (1) It includes time; indeed, a true sustainability assessment must supply information over time, once time is in the basis of the sustainability concept expressed in [1]; (2) it includes not only the inputs feeding the system, but also considers the fluxes associated to the construction, decommissioning and harmful wastes. In this sense, the Life Cycle Assessment of the product is present. (3) The same basis (exergy) is used throughout the analysis, allowing a quantification of the irreversible depletion of natural resources. The main drawback is the large amount of data necessary to determine the thermo-ecological cost of each flux separately, specially the imported goods necessary to the installation. This is normally computed by an iterative process [90].

8. The triple bottom line revisited

Despite the great importance of socio-economic aspects in the sustainable development, the environment (one of the three pillars of the "triple bottom line" of sustainability) has a differential importance in relation to the other 2 pillars: it determines the metabolic (biophysical) nature of human activities. As a consequence, these activities are constrained by physical-based principles (natural laws). In a simple analogy, a human being needs many social, cultural, psychological and economic factors to attain well-being; but none of these factors are useful if the basic needs are not supplied: food, water and oxygen. With economic activities (including industry and the energy sector), the same occurs: low entropies resources are supplied, entropy generation occurs inside the systems and high entropy wastes are sent back to the environment. No other dimension of sustainable development can neglect this metabolic aspect ruled by physical-based laws.

Therefore, we think that a better representation of sustainable development is not a "triple bottom line", but rather hierarchical support structures, as illustrated in Fig. 3.

The use of thermodynamic insights about nature's contribution to human activities can provide a rigorous biophysical basis for evaluate sustainability. Coping with the surroundings (resources as inputs and wastes as outputs), the Second Law of Thermodynamics offers a physical background in the goal of evaluation the metabolic (and fundamental) dimension of sustainability.

9. Concluding remarks

Mass and energy are always conserved. The real indication of resources consumption is related to their useful value (exergy) in conducting process and maintaining suitable living conditions on Earth.

Natural and artificial systems are open systems supported by low-entropy flows. Within those systems, irreversible transformations take place, leading to entropy generation. It is this non-conservative aspect of entropy that enables it to be a rational and consistent measure of the unidirectional nature of anthropogenic processes.

The field of sustainability assessment can take advantage of the accumulated knowledge on thermodynamics to enlarge the sustainability discussion and include a multilevel and integrated approach.

We do not say that entropy is the answer to all sustainability assessment issues. We are stating that the biophysical dimension of sustainability must be addressed using the suitable natural law

(the entropy law). Tools that are able to cross different disciplines maintaining a coherent basis are useful in the multidisciplinary scenario required for sustainability assessment, and entropy is such a tool.

The thermodynamic insights must not be underestimated, as the empirical observation of nature has proved that natural systems obey thermodynamic laws, in all scales of size. If nature is ruled by these principles, it is, at least, recommended to use the same principles to evaluate the impact that technical systems have on environment, in terms of resources depletion, waste impacts and search for more sustainable processes.

Society can be a driving force for the search for more sustainable process and products. Indefinitely increasing the demands from the economic level cannot be, however, followed by indefinite answers from technological level. The technological innovation is ruled by natural laws of thermodynamics and the answers from a technological system for society demands are not unlimited. The technological improvements are constrained by physical laws. The social demands for more sustainable products and process must also include advances in the social level: changes on consumption levels, social values and evaluation of economic growth. All these issues are out of scope of this paper.

Crossing disciplinary boundaries is difficult and challenging, but the answers to the sustainability issue must not be sought inside isolated domains.

Appendix A. Examples of exergy balances.

The use of Eqs. (1)–(3) is showed in three cases: a boiler, a steam turbine and a throttling valve (Fig. A1).

The following data, taken from an industrial case previously reported by the authors [92], is used:

Boiler:

Fuel:

- Biomass (wood chips): 11.12 ton/h, LHV_{*}=2254 kcal/kg. Composition: C (28%), H (3.5%), O (27%), N (0.5%), ashes (0.5%), moisture (40%).
- Biomass (bark): 44.48 ton/h, LHV=1400 kcal/kg. Composition: C (17.8%), H (2.2%), O (18.4%), N (0.4%), ashes (1.2%), moisture (60%).
- Fuel oil: 0.9 ton/h, LHV=9450 kcal/kg. Composition: C (85.9%), H (10.9%), N (0.2%), S (0.95%) ashes (0 %), moisture (0%).

[*] *LHV = Lower Heating Value*

High pressure steam:
116.53 ton/h at 420 °C and 46 bar. Enthalpy: 3252.0 kJ/kg. Entropy: 6.7650 kJ/kg K.
Feed water:
130 °C, 75 bar. Enthalpy: 551.3 kJ/kg. Entropy: 1.6280 kJ/kg K.

Environmental parameters: 298.15 K and 1 atm.
The enthalpy and entropy of water at these conditions are 104.9 kJ/kg and 0.3672 kJ/kg K respectively.
Exergy of water (Eq. (2)):

$$\overline{b}_{water} = 551.3 - 104.9 - 298.15(1.628 - 0.3672) = 70.49\ \text{kJ/kg}$$

Exergy of steam (Eq. (2)):

$$\overline{b}_{steam} = 3252.0 - 104.9 - 298.15(6.765 - 0.3672) = 1239.60\ \text{kJ/kg}$$

Exergy of biomass:
The ratio of the chemical exergy to the LHV can be estimated using the following correlation with elementary composition [15]:

$$\beta = \frac{[1.0412 + 0.2160(z_{H_2}/z_C) - 0.2499(z_{O_2}/Z_C)[1 + +0.884(z_{H_2}/z_C)] + 0.0450(z_{N_2}/z_C)]}{1 - 0.3035(z_{O_2}/z_C)} \tag{A.1}$$

For wood chips and bark, the values are 1.1388 and 1.1445 respectively. The chemical exergy of the biomass can be estimated using the following expression [15] that takes into account the water content on the biomass (zw).

$$\overline{b}_{biomass} = (LHV_{biomass} + Lz_w)\beta_{biomass} + \overline{b}_w z_w \tag{A.2}$$

where L=the heat of vaporization of water (2440.0 kJ/kg) and $\overline{b}_w$ is the chemical exergy of water (55.0 kJ/kg). Using Eq. (A.2), the chemical exergy of wood chips and bark are, respectively, 11876.0 kJ/kg and 8413.9 kJ/kg.
Exergy of fuel oil:
A similar correlation for the ratio of the chemical exergy to the LHV is used [15]:

$$\beta = 1.0401 + 0.1728\left(\frac{z_{H_2}}{z_C}\right) + 0.0432\left(\frac{z_{O_2}}{Z_C}\right) + 0.2169\left(\frac{z_S}{z_C}\right)\left[1 - 2.0628\left(\frac{z_{H_2}}{z_C}\right)\right] \tag{A.3}$$

The calculated chemical exergy of fuel oil is 42071.3 kJ/kg.
The overall exergy balance (Eq. (3)):

$$\begin{aligned}&(11876\ (\text{kJ/kg})\text{ñ}11.12\ (\text{ton}/h) + 8414\ (\text{kJ/kg})\text{ñ}44.48\ (\text{ton}/h)\\ &\quad + 42071\ (\text{kJ/kg})\text{ñ}0.9\ (\text{ton}/h)\\ &\quad + 70.49\ (\text{kJ/kg})\text{ñ}116.53\ (\text{ton}/h))\text{ñ}10^3\ (\text{kg/ton})\\ &\quad = 1239.6\ (\text{kJ/kg})\text{ñ}116.53\ (\text{ton}/h) + \dot{I}\end{aligned}$$

$$\dot{I} = 113.32\ \text{MW}$$

This value represents the exergy destruction due to irreversible processes inside the boiler plus the exergy loss due to combustion gases and ashes outside the control volume.

This model has the following simplifications: no losses of feed water, no losses of heat for the environment (adiabatic control

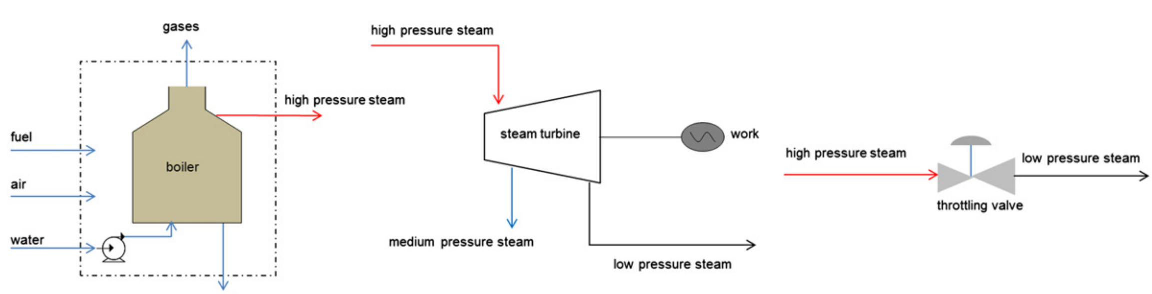

Fig. A1. Boiler, steam turbine and throttling valve with respective fluxes.

volume) and chemical exergy of air not considered (much smaller than the exergy of fuels).

Steam turbine:

– High pressure steam (HP): 270 ton/h at 420 °C and 46 bar. Enthalpy: 3252.0 kJ/kg. Entropy: 6.765 kJ/kg K
– Medium-pressure steam (MP): 90 ton/h at 280 °C and 12.5 bar. Enthalpy: 3001.0 kJ/kg. Entropy: 6.934 kJ/kg K.
– Low-pressure steam (LP): 180 ton/h at 230 °C and 4 bar. Enthalpy: 2923.0 kJ/kg. Entropy: 7. 299 kJ/kg K.

From the energy balance, $W^{\cdot} = 22.72$ MW. From the exergy balance (Eq. (3)), the total energy destruction due to the irreversible expansion of the steam is 9.22 MW.

In this technical system (a turbine), the production of work is possible due to the feed of a low entropy flux (high pressure steam). The ability of the high pressure steam to run the process is due to its departure from environment conditions (high pressure and temperature).

Throttling valve:

Contrary to the turbine example, the expansion of the steam does not perform any useful work ($W^{\cdot} = 0$). Considering an adiabatic process ($Q^{\cdot} = 0$), it can be showed by an energy balance that $\overline{h}_{inlet} = \overline{h}_{outlet}$. Therefore, the energy balance does not identify any losses: the input energy flow is equal to the output energy flow.

However, the use of Eq. (1) reveals a qualitative loss during the expansion process.

Eq. (1) gives

$$\dot{m}_{inlet} T_0 (\overline{s}_{outlet} - \overline{s}_{inlet}) = T_0 \dot{S}_g \tag{A.4}$$

The entropy on the outlet is greater than the entropy on the inlet (entropy generation). Considering a 23.28 ton/h of steam flow in the valve, the exergy destruction rate ($T_0 S^{\cdot}_g$) is 2.12 MW. If one consider that 1 MWh of energy has a price associated ($/MWh), there is an economic loss ($/h) associated to this entropy generation. However, no losses can be identified using an energy-based analysis.

Appendix B. Example of thermo-ecological cost calculation.

This example in a wind power plant is given by Szargut [24]. Annual operational time of the nominal power: 2000 hour/year; steel consumption per 1 MW of nominal power: 240 ton/MW; life time: 15 years; utilization efficiency of the steel scrap (after the wear of the installation): 0.35 and efficiency of electricity transformation and transmission: 0.9.

Considering that no harmful substances are delivered to the environment and that wind is a renewable form of energy, only the construction and decommissioning phase are taken into account. Also, neglecting all other materials used in construction or repairs, Eq. (5) becomes:

$$\begin{aligned}\rho_A &= \frac{1}{\tau}\left[\sum_m G_m \rho_m (1-u_m)\right] \\ &= \frac{(240/0.9)\ \text{ton}\tilde{n}58700\ \text{MJ/ton}\tilde{n}(1-0.35)}{15\ \mathit{year}\tilde{n}2000\ \text{h}/\mathit{year}\tilde{n}3600\ \text{s/h}} \\ &= 0.0943\ \text{MW}\end{aligned}$$

This means that to deliver 1 MW of electricity, 0.0943 MW of exergy is extracted from nature. In 1 MW of electricity there is 1 MW of exergy (the relation energy/exergy = 1 for electricity). Thus, the sustainability index is also equal to 0.0943. This example shows that even when renewable sources of energy are used, the ecological footprint due to its construction phase is also taken into account (the use and discharge of steel).

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